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STUDY OF DYEING OF WOOL PRETREATED TO PRODUCE CONTRAST EFFECTS

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Arun M. Parikh

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STUDY OF DYEING OF WOOL PRETREATED

TO PRODUCE CONTRAST EFFECT

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DEDICATED TO

MR. KENDAL WEISIGER

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TABLE OF CONTENTS

LIST OF TABLES

SUMMARY

This work is a continuation of an investigation initiated in the laboratories of the A. French Textile School at Georgia Tech, which resulted in the development of a new method for producing two-color effects on wool yarns or fabrics. The desired results were originally obtained by dyeing two samples of wool, each pretreated by a different method, in a buffered dyebath containing two carefully selected dyestuffs. Further work on this problem indicated that the same effect could be achieved by dyeing one treated and one untreated sample of wool in the same dyebath.

The work presented here consists of a study of the effect of the variables, in both the pretreatment and dyeing procedures, on the final results obtained.

The method of pretreatment was investigated first. Various pretreating agents were applied in different concentrations with the aid of a variety of acids, under controlled conditions of time, pH and temperature. It was established that the desired effect could be obtained by pretreating only one of the two samples used in the dyeing. After determining what appeared to be the optimum treatment for maximum contrast using one pair of dyes in the dyebath, the applicability of this treatment to a large variety of dye combinations was investigated.

During this phase of the work dyeings were made with one, two or three dyes in the dyebath.

The effect of the variables normally readily controllable in any dyeing operation -- dyestuffs used, ratio of dyes, dyebath ratio, effect of salt, etc. -- were investigated; and the light and wash-fastness of some of these dyeings were determined.

In the final phases of this work, attempts were made to improve the results obtained by varying the process in such a manner that maximum contrast consistent with best dyeing and minimum damage to the wool was effected.

Problems left unsolved and suggestions for further work are included.

CHAPTER I

INTRODUCTION

A new method for producing two-color and two-tone effects on woolen fabrics was developed by Davis (1). The desired results were attained by pretreating two samples with Synthratan ACA (a condensation product of a naphthalene sulphonic acid with formaldehyde), one in the presence of phenol, the other with phosphoric acid. These two samples were then dyed in a buffered dyebath containing two carefully selected dyes.

This work was extended by Anderson (2) who studied, spectrophotometrically, the change in concentration of two dyes and of Synthratan ACA in a dyebath during an actual dyeing. Anderson (2) also demonstrated the feasibility of obtaining the desired results by pretreating only one sample, and dyeing this in a bath with an untreated sample.

The work reported here is a continuation of the investigation initiated by Davis and extended by Anderson. The purpose of the work was to investigate further the variables in the process of dyeing treated and untreated wool two colors in the same dyebath and to develop, if possible, a simple, economical method for producing the desired results.

The method of pretreatment was investigated first. Various agents were applied with the aid of a variety of acids under controlled conditions of pH, time and temperature. After establishing what appeared to be the optimum pretreatment for maximum contrast using one pair of dyes, the applicability of this treatment to a large variety of dye combinations was investigated. During this phase of work, dyeings were made with one, two or three dyes in the dyebath.

The effect of the variables normally readily controllable in any dyeing operation -- dyestuffs used, ratio of dyes, dyebath ratio, effect of salt, etc. -- were investigated and finally, the light and wash-fastness of some of these dyeings were determined.

CHAPTER II

INSTRUMENTS AND EQUIPMENT

The following is a list of some of the equipment utilized in conducting the work described herein.

1. Fade-Ometer (3).
2. Launder-Ometer (4).
3. Hosiery Dyeing Machine manufactured by Smith Drum Company, Philadelphia, Pennsylvania.
4. Fletcher Dryer manufactured by Fletcher Works, 247 Glenwood Avenue, Philadelphia 40, Pennsylvania.
5. Beckman pH Meter, Model No. H2.
6. J-2 Scott Vertical Tester (3 inch jaw) (5).

CHAPTER III

EXPERIMENTAL PROCEDURE

The Pretreatment

Effect of Acids.--Samples (1.0 gram samples, weighed without previous conditioning, were used throughout this work) were treated for one hour at the boil in 100:1 baths containing 10 per cent (o.w.f.)* Synthratan ACA and some acid. (See Table 1 for details concerning type and amount of acid used.) The effect of each pretreatment was determined by dyeing one treated sample 24 hours after pretreatment and one untreated sample (1.0 gram each) in a 100:1 dyebath containing 3 per cent (o.w.f.)* of Fast Acid Yellow G. S. and 1 per cent Alizarine Sapphire F. S. The samples were entered at room temperature into an unbuffered dyebath. The dyebath was heated gently so that the temperature reached 165° F within 15 minutes and was stirred vigorously with a glass rod. Cuttings from each of the samples were taken when the temperature reached 165° F, and rinsed. The temperature of the dyebath was raised to 180° F from 165° F within 15 minutes. Samples were stirred by hand, and cuttings were taken at 180° F. The bath was then heated to the boil during 15 minutes, and the samples were then removed, rinsed and dried at room temperature.

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*All pretreating agent and dye percentages are based on weight of fabric.

Table 1. Acids Used in the Pretreatment

Name of Acid	Volume ml.	Acid Strength %
Sulfuric Acid	1	95
Phosphoric Acid	5	85
Phenol	4	95
Acetic Acid	9	99
Formic Acid	7	90
Sulfuric Acid	2	95
Sulfuric Acid	3	95
Sulfuric Acid	4	95
Phosphoric Acid	10	85
Phosphoric Acid	15	85
Phosphoric Acid	20	85

Pretreating Agents.--Samples* (1.0 gram) were treated at the boil for one hour in a 100 ml. bath containing 10 ml. of 85 per cent phosphoric acid. Four different agents at various concentrations were used.

Each of the pretreatments was evaluated by the same dyeing procedure as in the case of "Effect of Acids."

The results obtained are summarized in Table 4 in the Appendix.**

In one experiment a sample pretreated for one hour at the boil in a 100:1 dyebath containing only 1 per cent (o.w.f.) Decomine was dyed in a 100:1 bath with a sample pretreated with 40 per cent Synthratan in usual manner.

Effect of Pretreatment on Strength of Woolen Fabric.--Twelve (6 1/2" x 1") untreated samples of wool blanket material supplied by Peerless Woolen Mills were cut for strip tests as recommended by the A. S. T. M. (5). Samples were dried for four hours in an oven at 60° C, then left for 24 hours in a room at 65 per cent relative humidity and 70° F.

Six of these samples were pretreated with 60 ml. of phosphoric acid (85 per cent) and 10 per cent Synthratan ACA in a 100:1 bath at the boil for one hour, then dried and conditioned as described above.

Strength tests on the treated and untreated samples were run on a Scott Vertical Tester. The jaws, measuring 3" x 1", were set three inches apart.

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*All samples used in this work were of 1.0 gram each.

**Tables 4 through 17 will be found in the Appendix.

Results of these tests are recorded in Table 5.

Time of Pretreatment. --Samples were pretreated at the boil in 100:1 baths containing 40 per cent Synthratan ACA and 10 ml. of 85 per cent phosphoric acid for the following times: 30 minutes, 45 minutes, and 60 minutes.

The effect of each pretreatment was determined by dyeing one treated sample and one untreated sample in a 100:1 dyebath containing 3 per cent Fast Acid Yellow G. S. and 1 per cent Brilliant Scarlet 3R. Samples were entered in a dyebath buffered* at pH 3.0. The dyebath was heated gently so that the temperature reached the boil within 15 minutes. Samples were dyed at the boil for 30 minutes.

Results are shown in Table 6.

Stability of Pretreatment. --Pretreatment was effected by boiling for one hour in a 100:1 bath containing 10 ml. of 85 per cent phosphoric acid for each gram of wool being treated, and 40 per cent Synthratan ACA.

The ability of the pretreated samples to resist take up of dye was determined at various time intervals after pretreatment by dyeing under controlled conditions with an untreated sample in a bath containing two dyestuffs. Dyeings were carried out (a) immediately after pretreating and after (b) one, (c) two, (d) three, (e) seven and (f) seventeen days.

The contrast obtained is described in "Results" chapter.

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*In all work described herein, pH adjustment was effected by using either a 40 per cent solution of diammonium phosphate or an 8.5 per cent solution of phosphoric acid.

Use of Dye as a Pretreating Agent

Pretreatment.--A one gram sample was dyed in a 40:1 dyebath containing 10 per cent sodium sulfate (decahydrate), 1 per cent sulfuric acid, and 2 per cent Brilliant Scarlet 3R. The sample was entered into the dyebath at room temperature, heated slowly to the boil (the process requiring 15 minutes), and then dyed at the boil for 45 minutes.

Dyeing.--The above pretreated sample and an untreated sample were dyed in a 40:1 dyebath containing 2 per cent Fast Acid Yellow G. S. and 2 per cent Fast Blue G. L., 6 per cent acetic acid, 10 per cent sodium sulfate (decahydrate). Samples were entered at 120° F, heated to the boil (the process requiring 15 minutes) and dyed at the boil for 45 minutes.

Dyeing

Dyestuffs.--All dyes used in this work were furnished by National Aniline Division, Allied Chemical and Dye Corporation. For purposes of the work described herein, all of these dyestuffs were assigned a group number on the basis of one of the five methods of application recommended by the manufacturer in its publication entitled National Acid Dyes on Wool (6). This method of classification is summarized in Table 2.

Effect of Time and Temperature on Dyeing in an Unbuffered Dyebath.--Samples were treated for one hour at the boil in 100:1 baths containing 40 per cent Synthratan ACA and 10 ml. of 85 per cent phosphoric acid.

The effect of time and temperature was determined by dyeings

Table 2. Dyestuffs Used

Group No.	Recommended Method of Application: Initial pH of dyebath adjusted with	National Aniline Name	New Color Index (7) Name
I	1-4% H_2SO4, 66° Be.	Alizarine Sapphire FS.	Acid Blue 45
I	"	Fast Wool Yellow 3GL.	Acid Yellow 11
I	"	Fast Wool Red BL.	Acid Red 34
I	"	Fast Wool Red GL.	Acid Red 37
I	"	Alizarine Sapphire BLN.	Acid Blue 45
I	"	Resorcine Yellow	Acid Orange 6
I	"	Alizarine Sapphire SE.	Acid Blue 43
I	"	Quinoline Yellow	Acid Yellow 3
II	2-8% Acetic Acid, 28%	Brilliant Scarlet 3R.	Acid Red 18
II	"	Acid Brilliant Red GL.	Acid Red 106
III	1 1/2 to 6% Acetic Acid, 28%	Fast Acid Yellow GS.	- - - - -
III	"	Milling Yellow NGS.	Acid Yellow 44
III	"	Wool Fast Blue GL.	Acid Blue 102
V	2-5% Ammonium Acetate	Milling Navy Blue 4B.	Acid Black 26

performed as described above under "Effect of Acids." Dyeings were conducted for 5, 10, 15, 20 and 30 minutes at each of the following temperatures: 150, 160, 165, 175 and 185° F. Results based on a comparison of swatches cut from the dyeings are given in Table 7.

Effect of pH.--Dyeings at different pH's as noted in Table 3 were carried out as described in the preceding section.

Results of all experiments except those conducted at the boil are in Table 8.

Effect of Dye Concentration.--The effect of different concentrations of the two dyes on contrast was determined by dyeing samples pretreated as described above in the section entitled "Effect of Time and Temperature on Dyeing in an Unbuffered Dyebath." Different proportions of Fast Acid Yellow G. S. and Alizarine Sapphire F. S., as shown in Table 9, were tried and dyeing was carried out at 150° F for 30 minutes at pH 2.5 in 100:1 dyebaths.

Results are also included in Table 9.

Effect of Dyebath Ratio.--Using samples pretreated as in the section on "Effect of Time and Temperature on Dyeing in an Unbuffered Dyebath," dyeings were conducted at pH 2.5 for 30 minutes at 150° F, using 3 per cent Fast Acid Yellow G. S. and 1 per cent Alizarine Sapphire F. S. The dyebath ratio was varied as shown in Table 10, which also includes the results obtained.

Table 3. pH and Temperature Used in Study of Effect of pH

pH	Temperature in °F
2.1	150, 165, 175
2.5	150, 165, 175
3.0	150, 165, 175
3.5	165, 175, 180
3.9	165, 175, 180
4.5	150, 160, 165, 175, 185
5.0	150, 160, 165, 175, 185
5.5	150, 160, 165, 175, 185

Effect of pH on Levelness.--The effect of pH on levelness was determined by dyeing one pretreated (as in section on "Effect of Time and Temperature on Dyeing in an Unbuffered Dyebath") and one untreated sample in a 100:1 dyebath containing 3 per cent Fast Acid Yellow G. S. and 1 per cent Brilliant Scarlet 3R at the boil for 30 minutes. Each dyebath was raised to the boil in 15 minutes. The initial pH of each dyebath was adjusted (after entering the wool) to one of the values shown in Table 11 by the addition of phosphoric acid or diammonium phosphate.

Results are given in Table 11.

Effect of Changing the pH During Dyeing on Levelness.--All dyeings were done as mentioned above in the section, "Effect of pH on Levelness," except the pH of the dyebath was varied during the dyeing. Dyeing was carried out for 15 minutes at 150° F at an initial pH of 6.0, 5.5, or 5.0, then lowered to 2.5 or 3.0, and dyeing was continued for an additional 15 minutes at the boil.

Results are shown in Table 12.

Effect of Salt.--The effect of salt on levelness was determined by conducting a series of dyeings as described in the section on "Effect of pH on Levelness." Various percentages of Glauber's salt (sodium sulfate decahydrate) were added to the dyebath before the wool was entered. pH adjustment was made after the wool was placed in the dyebath, with either diammonium phosphate or phosphoric acid.

Results of this series of experiments are given in Table 13.

Effect of Salt and a Change in pH.--Pretreatment and dyeing in this section were done as described above under "Effect of pH on Levelness" with the following exceptions: 10 per cent Glauber's salt (o.w.f.) was added to each dyebath before the wool was entered. The initial pH was adjusted (after entering the sample) to the values given in Table 14. After dyeing for 15 minutes at 150° F, the pH was lowered to 3.0, and dyeing was continued for 15 minutes at the boil.

Results are given in Table 14.

Dyeing with Only One Dye.--Eight dyeings of treated (as in section on "Effect of pH on Levelness") and untreated wool samples were carried out using 4 per cent of only one dye in a 100:1 dyebath for 30 minutes at 180°F at a pH of 2.5. Some dyes from Group I (Alizarine Sapphire F.S., Fast Wool Yellow 3GL., Fast Wool Red GL., Alizarine Sapphire BLN, Fast Wool Red BL, and Resorcine Yellow); one dye from Group II (Brilliant Scarlet 3R.); and Fast Acid Yellow G.S. (a Group III dye) were used.

Results are given in Chapter IV.

Use of Various Combinations of Dyes to Determine Range of Colors Available.--Treated (as in "Effect of pH on Levelness") and untreated samples were dyed in 100:1 dyebaths, each containing two dyes from different groups. Different pairs of dyes were tried at various temperatures and pH values as shown in Table 15. Each dyeing was carried out for 30 minutes at the temperature indicated.

Effect of Relative Affinity of Dyes on Levelness.--The four dyeings in this series were carried out as in the section, "Effect of pH on Levelness," except that the dyebath was adjusted to an initial pH of 3.0. Different pairs of dyes were tried as shown in Table 16. In each case 3 per cent Milling Navy Blue 4B (Group V) and 1 per cent of the dye of the lower group number was used.

Larger Scale Dyeings.--In order to determine the applicability of the method of obtaining contrast dyeings to larger samples, dyeings were carried out in a Smith Drum Hosiery Dyeing Machine.

One-half pound of knitted wool cloth and one-half pound of wool blanket material were treated for one hour at 206° F in 45.4 liters (100:1 bath) of water containing 4.54 liters of 85 per cent phosphoric acid and 136.2 grams (30 per cent o.w.f.) of Tamol N. The samples were then rinsed with water and dried overnight at room temperature.

The knitted goods treated as above were dyed with one-half pound of untreated knitted material in 45.5 liters of dyebath (100:1 liquor ratio)containing 4.54 gms. (1 per cent o.w.f.) of Alizarine Sapphire F. S., 13.62 gms. (3 per cent o.w.f.) Fast Acid Yellow G. S., and sufficient phosphoric acid (19 ml. of 85 per cent) to bring the pH to 2.5. The bath was heated to 206° F (the process requiring 15 minutes) and dyed at that temperature for 30 minutes.

The dyed sample was rinsed with water, centrifuged to remove excess liquid and dried at room temperature.

The wool blanket material treated as above was dyed with one-half pound of untreated material in 45.4 liters of dyebath (100:1 liquor ratio) containing 4.54 gms. (1 per cent o.w.f.) of Brilliant Scarlet 3R, 13.62 gms. (3 per cent o.w.f.) Fast Acid Yellow G. S., and sufficient phosphoric acid (5 ml. of 85 per cent) to bring the pH to 3.0. The bath was heated to 206° F during 15 minutes and dyed at that temperature for 30 minutes. The dyed samples were rinsed with water, centrifuged and dried at room temperature.

Fastness Tests

Light Fastness.--A series of ten dyeings was made to obtain samples for light fastness testing.

Pretreatment was the same as mentioned in section on "Effect of pH on Levelness."

Dyeing Procedure.--All dyeings were performed with two 1.0 gram samples, one treated, the other untreated. The 100:1 dyebaths were adjusted initially to a pH of 2.5 and dyeing was carried out for 30 minutes at the temperature indicated in Table 17.

The twenty samples, two from each dyeing, thus obtained were tested for light fastness in the Fade-Ometer (4). Exposures were made for 5, 10, 15 and 20 hours.

Results of this are in Table 17.

Wash-Fastness.--To determine fastness to washing, the samples dyed in the Smith Drum Machine (described in the section on "Larger Scale Dyeing") were used.

This test was carried out using "Tentative Test Method" 38-45 recommended by the American Association of Textile Chemists and Colorists (5).

CHAPTER IV

RESULTS

Pretreatment

Recommended Methods.--On the basis of the work reported here, the following is a recommended method for pretreating a sample (with a colorless dye) to be dyed with an untreated sample in order to obtain maximum color contrast: Boil for 45 minutes in a 100:1 bath containing 10 ml. of 85 per cent phosphoric acid for each gram of wool being treated, and either 40 per cent Synthratan ACA or 30 per cent Tamol N (o. w. f.).

Pretreatment may also be effected by dyeing a sample with a dyestuff, following the manufacturer's recommended procedure.

Effect of Acids.--(See Chapter III, Table 1) It was observed that samples treated with formic acid, acetic acid or phenol and Synthratan ACA did not resist the dye of lower group number, while samples treated with phosphoric acid or sulfuric acid and Synthratan ACA resisted the dye of lower affinity (lower group number). Samples dyed in the presence of 1 ml. of sulfuric acid and 10 per cent Synthratan ACA exhausted the dyebath more completely, at a lower temperature, than samples treated with 10 ml. of phosphoric acid (85 per cent) and 10 per cent Synthratan ACA. Pretreatment with phosphoric acid and Synthratan ACA gave better contrast than pretreatment with sulfuric acid and Synthratan ACA.

Samples treated with 10 per cent Synthratan ACA and more than 2 ml. of sulfuric acid or 10 ml. of phosphoric acid took the dye of lower affinity. Use of 10 ml. of phosphoric acid gave better results than 7 ml. or 8 ml. of phosphoric acid. Pretreatment with 10 ml. of phosphoric and 10 per cent Synthratan ACA gave the best contrast at 165° F. At the boil, contrast was poor but levelness was better than that obtained at lower temperatures.

Pretreating Agents.--As shown in Table 4, 40 per cent Synthratan ACA was the most effective concentration of this agent. The following percentages of Synthratan ACA are listed in decreasing order of effectiveness: (1) 40 per cent, (2) 45 per cent, (3) 30 per cent, (4) 10 per cent, (5) 50 per cent.

Thirty per cent Tamol N and 10 c.c. of phosphoric acid gave the best result in the Tamol series. Percentages of Tamol N listed in decreasing order of effectiveness are as follows: (1) 30 per cent, (2) 50 per cent, (3) 10 per cent.

In the Naccotan A series it was found that 50 per cent gave the best result. The following percentages of Naccotan A are listed in decreasing order of their effectiveness: (1) 50 per cent, (2) 40 per cent, (3) 30 per cent, (4) 10 per cent. Fifty per cent of Naccotan A was not as good as 30 per cent Tamol N or 40 per cent Synthratan ACA. Thirty per cent Tamol N was as good as 40 per cent Synthratan ACA.

It was found that 10 per cent or 1 per cent of Decomine did not aid in producing contrast. The use of Decomine increased the rate of exhaustion of both dyes from the dyebath in both instances in which Decomine pretreated samples were used. In neither case was there any appreciable difference in the color of the two samples dyed in the same dyebath.

Effect of Pretreatment on Strength of Wool Fabrics.--As shown in Table 5, 10 ml. of 85 per cent phosphoric acid and 10 per cent Synthratan ACA caused a 7.3 per cent loss in strength.

Time of Pretreatment.--As shown in Table 6, pretreatment for 45 minutes was as satisfactory as 60 minutes of pretreatment. Pretreatment for only 30 minutes did not give as good contrast as the two cases above.

Stability of Pretreatment.--The series of experiments conducted to determine the ability of treated samples to resist dye at various time intervals after pretreatment was effected indicated that even after seventeen days contrast between treated and untreated samples was obtained. However, the shade obtained was not the same in each case.

Use of Dye as a Pretreating Agent.--The use of a dyestuff as a resist agent proved to be successful. The treated sample was dyed black, and the untreated sample was dyed green.

Dyeing

Recommended Method.--Dye a pretreated sample and an untreated sample in a 100:1 dyebath containing 3 per cent (o. w. f.) of the dye with the higher group number (higher affinity) and 1 per cent (o. w. f.) of the dye with the lower group number (lower affinity) at the boil for 30 minutes at a pH of 3.0 (adjusted with phosphoric acid).

Effect of Time and Temperature on Dyeing in an Unbuffered Dyebath. -- The pH of an unbuffered dyebath containing 3 per cent Fast Acid Yellow G. S. and 1 per cent Alizarine Sapphire F. S. was 3.3. As observed in Table 7, at 150° F little or no contrast was obtained. At 165° F contrast was good and the dye with the higher group number was completely exhausted from the dyebath in 30 minutes.

As shown in Table 7, the best contrast in this series was obtained when dyeing was continued for 10 minutes at 165° F. At 175° F the dye with the lower group number began to exhaust and was taken up by the treated sample; there was little contrast. At 185° F both dyes dyed the treated and untreated samples and little contrast was obtained. At the boil, the results were similar to that obtained at 185° F; however, levelness was better at the higher temperature.

Effect of pH. --Neither the treated nor the untreated samples took the dye of lower group number when the pH of the dyebath was 5.5, 5.0, or 4.5. As a result, no contrast was obtained at these pH values.

As shown in Table 8, when the pH of the dyebath was 2.1, better contrast was obtained in the series of dyeings made at 150° F than those carried out at 165° F or 175° F.

The best contrast was obtained when the pH of the dyebath was 2.5 and samples were dyed for 30 minutes at 150° F. When dyeing at a pH of 2.5, at a temperature of 150° F, 165° F or 175° F, the higher the temperature, the poorer the contrast obtained.

When the pH of the dyebath was 3.0, best contrast was obtained when treated and untreated samples were dyed for 20 minutes at 165° F.

When the pH of the dyebath was 3.5, the 175° F series of dyeings gave better result than the 165° F or 185° F series. At a pH of 3.9, better contrast dyeings were obtained at 185° F than at 165° F or 175° F.

It was observed from this series of experiments that the higher the pH, the better the resist at higher temperatures. Best contrast was obtained by dyeing the treated and untreated samples for 30 minutes at a temperature of 150° F at a pH of 2.5.

In the experiments conducted at the boil, at all pH's above 3.9, essentially none of the dye of lower group number exhausted from the bath in 10 minutes. Therefore, contrast between treated and untreated samples was not obtained in this time interval. At pH 2.1, 2.5, 3.0, 3.5 or 3.9, both the treated and untreated samples took both dyes in the bath when dyeing was conducted at the boil for 10 minutes. In these cases a color difference, best described as two tones of the same color, was obtained.

<u>Effect of Dye Concentration</u>.--As seen from Table 9, 3 per cent of the

dye with the higher group number, and 1 per cent of dye with lower group number gave the best contrast. When the percentage of the dye of higher affinity was increased, its rate of exhaustion apparently decreased. Because the treated sample resisted the dye of lower affinity, increasing the percentage of the higher group number dye resulted in poor contrast. The use of 4 per cent of dye with the higher group number and 1 per cent of dye with lower group number gave fairly good contrast.

Effect of Dyebath Ratio.--As seen from Table 10, the 100:1 dyebath ratio gave good contrast. The results obtained with an 80:1 ratio gave results similar to that obtained with the 100:1 dyebath ratio.

It was observed that by decreasing the dyebath ratio, the contrast obtained was poor, and the dye with higher group number exhausted more rapidly.

Effect of pH on Levelness.--As seen from Table 11, the contrast was good at a dyebath pH of 3.0 and the levelness was fair; when the pH of the dyebath was raised to 3.5, the contrast was good and levelness was poor. At a pH of 4.0, little contrast was obtained and the levelness was fair.

When dyeing was begun at higher pH's, then lowered to 2.5 and dyeing continued, the contrast was good, but the levelness was poor, as shown in Table 12. Lowering from a pH of 5.0 to a pH of 3.0 gave no contrast.

Effect of Salt.--As shown in Table 13, it was observed that with 10 per cent sodium sulfate (decahydrate) in a dyebath at a pH of 3.0, good contrast was obtained. When the pH of dyebath was 3.5, the contrast was good, but the levelness was poor. In a dyebath at pH 2.5, containing 10 per cent Glauber's salt, there was little contrast and poor levelness. When the pH of the dyebath was 4.0, the contrast was poor, but the levelness was fair.

Amounts of salt in excess of 10 per cent did not improve either contrast or levelness.

The presence of salt did not help so far as levelness was concerned, even when the pH of dyebath was changed during the dyeing.

Dyeing with Only One Dye.--When only one dye from Group I or Group II was used for dyeing treated and untreated samples in the same dyebath, marked differences in shade on the treated and untreated samples were obtained. The Group III dye was taken up by both samples eventually to the same extent.

Use of Various Combinations of Dyes Determine Range of Colors Available.--The experiments demonstrated that it is possible to obtain a wide range of colors.

Effect of Relative Affinity of Dyes on Levelness.--Levelness is improved when the two dyes used are selected from groups which are as widely separated as possible.

Note that the Group III dye Fast Acid Yellow G. S. dyed both a treated and untreated sample when used alone at a pH of 2.5 in a bath at 150° F; however, when used in combination with the Group V dye Milling Navy Blue 4B at a pH of 3.0 at the boil, the Group V dye dyed both samples while the Group III dye was resisted by the treated sample.

Larger Scale Dyeing.--The results obtained from the one pound dyeings carried out on the Smith Drum Machine were quite satisfactory. This demonstrated the applicability of the recommended method for pretreatment and dyeing to larger scale work.

Light Fastness.--It was found that untreated samples possessed better light fastness than treated samples. It was also found that samples dyed at the boil had better light fastness than samples dyed at 150° F.

Wash Fastness.--It was found that in the case of dyeing with Brilliant Scarlet 3R and Fast Acid Yellow G. S., the treated samples showed appreciable change (fading) while untreated samples showed only a slight change. In the case of dyeing with Alizarine Sapphire F. S. and Fast Acid Yellow G. S., both treated and untreated samples showed only a slight change, but both stained the undyed sample.

CHAPTER V

DISCUSSION OF RESULTS

Mechanism of the Acid Dyeing of Wool. --The mechanism of the acid dyeing of wool is explained by Vickerstaff (9) as follows:

> . . . a normal acid dyebath contains a mixture of hydrogen ions from the acid, sodium ions from both dyesalt and any added electrolyte and dye anions and other anions from the added acid and electrolyte. . . . when wool is placed in such a dyebath, the hydrogen ion will be adsorbed by the carboxyl group in the fibers. The dyebath, however, contains a mixture of anions, but in general the dye anions will be very much larger than inorganic anions and will diffuse much more slowly. . . . the inorganic anions will be adsorbed by the fiber before the dye ions. Equilibrium with the hydrogen ions is quickly attained, but the chloride ions after reaching a maximum adsorption, then leave the fiber as the more slowly moving dye ions are adsorbed. In other words the dye ions on entering the fiber displace an equivalent amount of chloride ions.

This mechanism is illustrated by Vickerstaff as follows:

$$\begin{array}{ccccccccccc}
NH_3^+ & & & & NH_3^+ & & & & NH_3Cl & & & & NH_3D & & \\
| & & & & | & & & & | & & & & | & & \\
W & + & H^+ & \longrightarrow & W & + & Cl^- & \longrightarrow & W & + & D^- & \rightleftharpoons & W & + & Cl^- \\
| & & & & | & & & & | & & & & | & & \\
COO^- & & & & COOH & & & & COOH & & & & COOH & &
\end{array}$$

Derbyshire and Peters (10) state that the great affinity of dye for wool arises from other types of bonding between the dye molecule and the fiber, such as hydrogen bonding and Van der Waal's forces which do not exist in the case of inorganic anions.

Pretreatment

Effect of Acids.--The relative amounts of acid used in each case was based on the ionization constants of these acids. Ionization constants of the acids used are as follows (8):

Name of Acid	Ionization Constant K	Temp.
Sulfuric acid	4×10^{-1} (?)	25° C
Phosphoric acid	1.1×10^{-2} (1 H)	18° C
Phenol	1.3×10^{-10}	25° C
Formic acid	2.14×10^{-4}	25° C
Acetic acid	1.86×10^{-5}	25° C

Vickerstaff (11) points out that undissociated weak organic acids and phenol exert a strong swelling action on wool, due probably to hydrogen bonding of these compounds to the amide groups in the fiber. Thus the pretreatment with phenol, formic or acetic acid resulted in the adsorption of the weak acid but not of the Synthratan. It is assumed that adsorption of Synthratan can be effected only in the presence of strong acids, which back titrate the ionized carboxyl groups in the wool and thereby creates sites at which the colorless dye anion may be adsorbed. Thus the necessity for using an acid such as phosphoric or sulfuric in the pretreatment is explained.

It was found that the use of more than 2 ml. of 95 per cent sulfuric acid or 10 ml. of 85 per cent phosphoric acid per 100 ml. of pretreating bath caused an increase in the amount of dyestuffs taken up by the treated sample in a contrast dyeing experiment. This can be explained on the basis of work described by Elode and Bohme (12) and earlier by Pelet-Jolivet and Sigrist (13) who found, in dyeing wool from a bath containing a limited quantity of dye, that the amount of dye adsorbed did not increase continuously with increasing addition of mineral acid but passed through a maximum, thereafter decreasing with decreasing dyebath pH. By increasing the amount of acid, the first effect was to increase the number of hydrogen ions adsorbed by the fiber and thus the dye uptake when all the carboxyl groups in the fiber were unionized; however, further addition of acid could not produce further hydrogen ion adsorption, but the increasing number of anions competed with dye ions for the sites and reduced the dye ion adsorption.

Effect of Pretreating Agents

Anionic Agent (colorless dye).--The pretreating agents used were: Synthratan ACA, a condensation product of a napthalene sulfonic acid with formaldehyde; Tamol N, a napthalene sodium salt of a condensed aryl organic acid; Naccotan A, a sodium salt of sulfonated napthalene condensate product (14).

Elliot and Speakman (15) mentioned the use of compounds of these types in their work which was devised to develop improved resist processes for wool.

The relative affinities of the two dyes and of the pretreating agent have been assumed to be a major factor in determining the success of this method of obtaining contrast dyeings. The simplest explanation of the effect of the resist agent is to assume that its affinity for wool lies between that of the two dyes used in the dyebath. During dyeing, the dye of higher affinity is able to displace the pretreating agent, and dye both the treated and untreated samples. The dye of lower affinity, being unable to replace the reserve agent, dyes only the untreated wool. As will be shown below, however, the true explanation is not this simple.

Cationic Agent as a Pretreating Agent.--Hindle (16) recommended the use of cationic agents such as Decomine (a mixture of non-ionic and anionic agents (17)) for obtaining two color effects when dyeing blends of Acrilan and wool. It was therefore assumed that dyeing two wool samples in the same bath, one pretreated with Decomine and the other pretreated with Synthratan ACA might improve the contrast obtained, since the Decomine was used in Hindle's work to increase the uptake of the dye by the wool.

Time of Pretreatment.--As mentioned before, Synthratan ACA is assumed to be a colorless dye. Therefore, as in the case with any dyestuff, sufficient time must be allowed in order to permit the dye to penetrate the fiber and attach itself to the wool molecule. Under the conditions of pretreatment used in this work, 45 minutes is apparently a minimum time required to obtain maximum adsorption of the pretreating agent.

Dyeing

Effect of Time and Temperature on Dyeing in an Unbuffered Dyebath. -- In the series of experiments conducted in an unbuffered dyebath, the effect of time and temperature on contrast was studied. It was found that below 165° F, the treated sample took only one dye (the dye of higher affinity); the untreated sample took both dyes in the dyebath. Above this temperature, the dye of lower affinity began to exhaust on to the treated sample. As time and temperature were increased, the difference in color between the treated and untreated samples became less.

This result may be interpreted in several ways. One possible explanation is that for the particular dyes used, 165° F is a critical temperature below which the rate of exhaustion of the dye of lower affinity is very slow.

Another suggested explanation may be based on a possible change in relative affinities of the pretreating agent and the dye of lower affinity in the bath as the temperature is increased. Below 165° F the treated sample adsorbed essentially none of the dye of lower affinity, even in 30 minutes. This may be interpreted as a result of either the inability of the dye to replace the Synthratan ACA at this temperature or of a very slow rate of replacement at the temperature.

Effect of pH.--Speakman and Coke (18) have stated that neutral dyeing in the presence of sodium sulfate alone is detrimental to wool; therefore, a pH of 7.0 or higher was not tried.

Vickerstaff (19) has given a very general type of classification of acid dyes based on their method of application, leveling, and wet fastness of the final dyeing. Acid dyes are in general applied in the pH range 2.0 to 6.0, depending upon the class to which they belong. Therefore, all dyeings were conducted within this pH range.

There was no two color effect when dyeing at a pH between 4.0 and 6.0. When the pH was 4.0 or higher the dye of lower group number did not dye either of the samples. At 150° F, with low pH (between 2 and 3), good contrast was obtained at higher temperature (175° F to boil); with higher pH (3 to 4), contrast was good, but not as good as that obtained at the lower temperatures. Vickerstaff states that "each dye has a critical pH above which little adsorption on wool takes places" (20). Hence it is necessary to bring the pH of the dyebath below this point, and this will necessitate a lower pH for dyes of lower group number. Vickerstaff further states that every dye has "an optimum pH range in which good exhaustion is combined with adequate leveling, and in general this range moves toward higher pH values with increasing anion affinity" (21). These facts are presented to explain the better contrast obtained at the lower pH of dyeing.

Microscopic examination of the treated and untreated samples was conducted. It was found that dyeing was not uniform and that levelness was poor. Vickerstaff (22), citing work by Peters and Lister, points out that rate of dyeing increases with decreasing pH. The rapid rate of dyeing at low pH is a possible explanation for the poor levelness obtained.

Peryman (23) recommends that the dyeing of wool should be carried out between pH 3 and 5, in order to minimize damage to the fiber. Therefore, in order to have good levelness and not to cause appreciable loss in strength of the wool, dyeing should be carried out at pH 3.0 and at the boil.

Effect of Dye Ratio.--Under the dyeing conditions of pH, time and temperature used in these experiments, there were apparently sufficient sites available for a limited amount of dye on the two samples of wool. When 2 per cent Fast Acid Yellow G. S. and 1 per cent Alizarine Sapphire F. S. were used, both dyes dyed both the treated and untreated samples. When the amount of yellow dye was increased to 3 per cent, all of the available sites in the treated sample were taken up by the yellow dye, thus preventing dye adsorption by the treated sample of the dye of lower affinity. As the amount of yellow dye was further increased, the dye of higher affinity occupied the available sites in both the treated and untreated samples. When 4 per cent yellow dye was used, a few sites for the blue dye remained in the untreated sample and these was taken up by the blue dye. When more than 4 per cent yellow dye was used all of the available sites in both samples were taken up by this dye.

Effect of pH and Temperature on Levelness.--(See Table 12) Vickerstaff (24) states, "A level dyeing is one in which two samples selected at random from different parts of the piece of cloth or batch are identical in color."

An attempt was made to dye the samples at high pH and at low temperature and then to lower the pH and continue the dyeing at the boil. These dyeings showed poor levelness. Unlevelness is associated with rapid dyebath exhaustion and slow diffusion within the fiber. Dyes of high affinity in general diffuse slowly. pH control is one of the most effective means by which uniform adsorption of acid dyes from solution can be obtained (25). This is the reason why the pH was controlled in this series of experiments. A common method for effecting uniform initial application of dye to the material is to lower the temperature of dyeing in the early stages by starting dyeing at 104° - 140°F and then raising the temperature to the boil to promote the maximum migration of dye within the fiber. For dyes of low affinity, this procedure is effective, but it is not true for dyes of higher affinity, as only little dyeing takes place below a critical temperature. This might explain why there was poor levelness in the series when dyeing was begun at low temperature and then raised to boil.

A method of retarding dyeing is to reduce the affinity of the dye for the fiber. This may be achieved by increasing the pH; for this reason a pH higher than 2.5 was tried. An attempt was also made to dye the samples initially at a low temperature and a high pH, then cool the dyebath and lower the pH, and continue the dyeing at the boil. This did not give any improvement in levelness. This was tried in order that the dye of high affinity might level first. There was little contrast as the dye with lower group number exhausted rapidly at the boil.

Effect of Salt and pH on Levelness.--Vickerstaff (26) states that it was found empirically that the addition of an inorganic salt such as Glauber's salt improves leveling, which suggests that the addition has produced a displacement of the distribution of dye between fiber and bath in favor of the latter. Final distribution of dye and inorganic anions will depend upon their relative concentration. If the concentration of sulfate ions in a dyebath is increased by the addition of Glauber's salt this will lead to leveling. As observed, addition of salt did not help. This is because in the case of dyes of higher group number, dyes are scarcely desorbed at all by the acid solution. The displacement reaction is governed not only by the concentration of the two competing ions, but also by their relative affinities for the fiber.

In the case of dyes with lower group number, increasing electrolyte concentration produces a considerable decrease in dye adsorption at low pH values, but above this critical pH the reverse effect takes place. As observed, there was only little contrast at pH 3.0 when the concentration of electrolyte was increased. If it is assumed that in this case pH of 3.0 was the critical pH, the results obtained agree with the theory.

The unlevelness may have been due to the colloidal properties of the dye of higher affinity. Speakman and Clegg (27) state that those dyes which give colloidal solutions are inferior in leveling properties to those giving molecularly dispersed solutions. It was observed that Fast Acid Yellow G. S. did not give clear aqueous solutions whereas Brilliant Scarlet 3R and Alizarine Sapphire F. S. did dissolve with the formation of clear solutions. This might explain the poor leveling of the dye of higher affinity.

Dyeing Pretreated Sample with Only One Dye.--The results obtained from dyeings done with only one dye in the bath indicate that two tones of the same color can be obtained when dyes from Group I and II are used. This effect can be explained on the basis that in the case of the treated sample, the dye has to displace the pretreating agent before it can become attached to the fiber. Dyeing of the untreated sample can proceed directly. Therefore, the rate of uptake of dye by the untreated sample is greater, and the untreated sample dyes a darker shade.

The fact that no contrast between the treated and untreated sample was obtained when a dye from Group III was used alone may be attributed to the much greater affinity of dyes of this Group. The very high affinity of Fast Acid Yellow G. S. permitted it to displace the Synthratan in the treated sample with great ease and therefore the treated sample took up the dye as readily as the untreated sample.

Effect of Relative Affinities of Dyes on Levelness. --The observed improvement in levelness when dyes from widely separated groups were used cannot be explained on the basis of evidence presently available.

Dyeing Various Combinations to Determine Range of Colors Available. --The generally good results obtained when a large range of dyestuffs was used indicates the general applicability of the recommended procedure.

CHAPTER VI

CONCLUSIONS

On the basis of the information obtained from this work, it is concluded that the following is the best method to produce two color effects by dyeing treated and untreated samples in the same dyebath: Dye a pretreated sample--pretreated at the boil for 45 minutes with 40 per cent (o. w. f.) Synthratan ACA in a 100:1 bath of a 17 per cent solution of phosphoric acid--and an untreated sample in a 100:1 dyebath containing 3 per cent (o. w. f.) of the dye with the higher group number (higher affinity) and 1 per cent (o. w. f.) of the dye with a lower group number (lower affinity) at the boil for 30 minutes at a pH of 3.0 (adjusted with phosphoric acid).

Each of three resist agents can be used, but Synthratan ACA and Tamol N give better results than Naccotan A. Sulfuric acid can be used in place of phosphoric acid for the pretreatment but weak acids such as formic, acetic or phenol are unsatisfactory.

In order to assume better uniformity of results, pretreated samples should be dyed between zero and 24 hours after pretreatment.

There is a relationship between the contrast obtained and the pH and temperature of dyeing. In the pH range 2 to 4, and the temperature range 150° F to the boil, good contrast is obtained when dyeing is effected between 140°F and 165°F. Best contrast is obtained when dyeings are carried out at low pH and temperature. Good contrast is obtained at low pH and high temperature. However, in order to obtain satisfactory contrast throughout the range of both pH and temperature it is necessary to increase the temperature as the pH increases.

It is desirable, in order to minimize degradation of the wool and to obtain the best dyeings with respect to contrast and fastness properties, to effect dyeings at the boil at a pH 3.0.

Low pH gives very good contrast at low temperature but levelness is very poor. The use of salt does not promote levelness, and contrast is sacrificed. Dyes from any two groups (see Chapter III under Dyeing) will give contrast but the more widely separated the groups from which the dyes are chosen, the better the levelness.

One dye can be used to obtain a two color effect with treated and untreated samples. A dye (instead of e.g. Synthratan ACA) can be used as a pretreating agent.

The pretreatment adversely affects the light-fastness of the treated samples.

CHAPTER VII

RECOMMENDATIONS

Search for a more effective pretreating agent is strongly recommended. It is also recommended that an attempt be made to effect the desired results by varying the dyestuffs and the conditions of dyeing in such a manner that pretreatment is unnecessary.

Further work should be done to find a method of dyeing and pretreating so that the maximum degree of levelness is attained. The reasons for the improved levelness when dyes from widely separated groups are used should be determined.

The spectrophotometric study initiated by Anderson should be extended in an attempt more fully to elucidate the mechanism of the reaction. Relative affinities of various acid dyes should be determined. Affinity values combined with a knowledge of tinctorial strengths (obtainable from the spectrophotometric studies recommended above) should make the selection of dyes for this work much easier. In connection with this work the necessity for using the pretreating agent on the sample treated with phenol should be determined.

The range of colors should be expanded. The use of a dyestuff as a pretreating agent should be further investigated.

The variables in the process should be further studied in order that better reproducibility may be obtained. Conditions which might improve the fastness of treated samples should be investigated.

A comparison of results obtained by the procedure recommended in this work (in which only one sample in the dyebath was treated) and the method developed by Davis and extended by Anderson (in which both samples in the bath were pretreated) should be made.

Attempts should also be made to effect the desired results with other classes of dyestuffs normally used in wool dyeing.

APPENDIX

Table 4. Effect of Pretreating Agents

Pretreatment	Dyeing Temp.	Minutes at Dyeing Temp.	Contrast
10% Synthratan ACA	165° F	5	Good
10% Synthratan ACA	175° F	5	Little
10% Synthratan ACA	180° F	5	Little
10% Synthratan ACA	At Boil	5	Little
30% Synthratan ACA	165° F	5	Little
30% Synthratan ACA	175° F	5	Good
30% Synthratan ACA	180° F	5	Little
30% Synthratan ACA	At Boil	5	Little
40% Synthratan ACA	165° F	5	Little
40% Synthratan ACA	175° F	5	Very Good
40% Synthratan ACA	180° F	5	Little
40% Synthratan ACA	At Boil	5	Little
45% Synthratan ACA	165° F	5	Little
45% Synthratan ACA	175° F	5	Good
45% Synthratan ACA	180° F	5	Little
45% Synthratan ACA	At Boil	5	Little
50% Synthratan ACA	165° F	5	Little
50% Synthratan ACA	175° F	5	Good

Continued

Table 4. (Cont'd.) Effect of Pretreating Agents

Pretreatment	Dyeing Temp.	Minutes at Dyeing Temp.	Contrast
50% Synthratan ACA	180° F	5	Little
50% Synthratan ACA	At Boil	5	Little
10% Tamol N	165° F	5	Little
10% Tamol N	175° F	5	Little
10% Tamol N	185° F	5	Good
10% Tamol N	At Boil	5	Little
30% Tamol N	165° F	5	Very Good
30% Tamol N	175° F	5	Very Good
30% Tamol N	185° F	5	Little
30% Tamol N	At Boil	5	Little
50% Tamol N	165° F	5	Good
50% Tamol N	175° F	5	Little
50% Tamol N	185° F	5	Little
50% Tamol N	At Boil	5	Little
10% Naccotan A	165° F	5	Little
10% Naccotan A	175° F	5	Little
10% Naccotan A	185° F	5	Little
10% Naccotan A	At Boil	5	Little

Continued

Table 4. (Cont'd.) Effect of Pretreating Agents

Pretreatment	Dyeing Temp.	Minutes at Dyeing Temp.	Contrast
30% Naccotan A	165° F	5	No Contrast
30% Naccotan A	175° F	5	Little
30% Naccotan A	185° F	5	Little
30% Naccotan A	At Boil	5	Little
40% Naccotan A	165° F	5	Little
40% Naccotan A	175° F	5	Good
40% Naccotan A	185° F	5	Little
40% Naccotan A	At Boil	5	Little
50% Naccotan A	165° F	5	Good
50% Naccotan A	175° F	5	Good
50% Naccotan A	185° F	5	Little
50% Naccotan A	At Boil	5	Little
10% Decomine	165° F	5	No Contrast
10% Decomine	175° F	5	No Contrast
10% Decomine	185° F	5	No Contrast
10% Decomine	At Boil	5	No Contrast

Table 5. Breaking Strength of Samples

	Sample No.	Breaking Load in Pounds
Untreated	1	28
	2	29
	3	28
	4	30
	5	28
	6	29
	Average = 28.6 lbs.	
Treated	1	26
	2	28
	3	27
	4	26
	5	26
	6	26
	Average = 26.5 lbs.	

Average of the untreated samples minus the average of treated sample = 2.1 lbs.

Per cent loss in strength = 7.3%.

Table 6. Effect of Time of Pretreatment on Contrast

Time (Minutes)	Contrast	Color	
		Treated	Untreated
30	Little	Orange Red	Red
45	Good	Orange	Red
60	Good	Orange	Red

Table 7. Effect of Time and Temperature on Contrast

Temperature	Time (Minutes)	Contrast	Color of Dyed Samples Treated	Untreated
150° F	5	None	Yellow	Yellow
	10	Little	Yellow	Yellowish Green
	15	Little	Yellow	Yellowish Green
	20	Little	Yellow	Yellowish Green
	30	Little	Yellow	Yellowish Green
160° F	5	Little	Yellow	Yellowish Green
	10	Little	Yellow	Yellowish Green
	15	Little	Yellow	Yellowish Green
	20	Good	Yellow	Greenish Yellow
	30	Good	Yellowish Green	Green
165° F	5	Good	Yellow	Greenish Yellow
	10	Very Good	Yellow	Green
	15	Good	Yellowish Green	Deep Green
	20	Good	Greenish Yellow	Deep Green
	30	Little	Pale Green	Deep Green
175° F	5	Little	Greenish Yellow	Green
	10	Little	Greenish Yellow	Green
	15	Little	Greenish Yellow	Green
	20	Little	Greenish Yellow	Green

(Continued)

Table 7. (Cont'd.) Effect of Time and Temperature on Contrast

Temperature	Time (Minutes)	Contrast	Color of Dyed Samples Treated	Untreated
175° F	30	Little	Pale Green	Deep Green
185° F	5	Little	Greenish Yellow	Green
	10	Little	Pale Green	Deep Green
	15	Little	Pale Green	Deep Green
	20	Little	Pale Green	Deep Green
	30	Little	Pale Green	Deep Green

Table 8. Effect of pH of Dyeing on Contrast

pH	Temp.	Time (Minutes)	Contrast	Color of Dyed Samples Treated	Untreated
2.1	150° F	5	Good	Yellow	Green
		10	Good	Yellow	Green
		15	Good	Yellow	Green
		20	Good	Yellow	Green
		30	Little	Pale Green	Deep Green
2.1	165° F	5	Good	Yellow	Green
		10	Little	Yellowish Green	Green
		15	Little	Greenish Yellow	Green
		20	Little	Pale Green	Deep Green
		30	Little	Pale Green	Deep Green
2.1	175° F	5	Good	Yellow	Green
		10	Little	Yellowish Green	Green
		15	Little	Greenish Yellow	Green
		20	Little	Pale Green	Deep Green
		30	Little	Pale Green	Deep Green
2.5	150° F	5	Good	Yellow	Green
		10	Good	Yellow	Green
		15	Good	Yellow	Green

(Continued)

Table 8. (Cont'd.) Effect of pH of Dyeing on Contrast

pH	Temp.	Time (Minutes)	Contrast	Color of Dyed Samples Treated	Untreated
2.5	150° F	20	Good	Yellow	Green
		30	Very Good	Yellow	Deep Green
2.5	165° F	5	Good	Yellowish Green	Deep Green
		10	Good	Yellowish Green	Deep Green
		15	Good	Yellowish Green	Deep Green
		20	Little	Pale Green	Deep Green
		30	Little	Pale Green	Deep Green
2.5	175° F	5	Little	Greenish Yellow	Green
		10	Little	Pale Green	Deep Green
		15	Little	Pale Green	Deep Green
		20	Little	Pale Green	Deep Green
		30	Little	Pale Green	Deep Green
3.0	150° F	5	Little	Yellow	Yellowish Green
		10	Little	Yellow	Yellowish Green
		15	Little	Yellow	Yellowish Green
		20	Good	Yellow	Green
		30	Good	Yellow	Green
3.0	165° F	5	Little	Yellow	Yellowish Green

(Continued)

Table 8. (Cont'd.) Effect of pH of Dyeing on Contrast

pH	Temp.	Time (Minutes)	Contrast	Color of Dyed Samples Treated	Untreated
3.0	165° F	10	Little	Yellow	Yellowish Green
		15	Little	Yellow	Yellowish Green
		20	Good	Yellow	Green
		30	Little	Greenish Yellow	Green
3.0	175° F	5	Good	Yellow	Green
		10	Good	Yellow	Green
		15	Little	Greenish Yellow	Green
		20	Little	Greenish Yellow	Green
		30	Little	Pale Green	Green
3.5	165° F	5	Little	Yellow	Greenish Yellow
		10	Little	Yellow	Greenish Yellow
		15	Little	Yellow	Greenish Yellow
		20	Good	Yellow	Green
		30	Good	Yellowish Green	Green
3.5	175° F	5	Little	Yellow	Greenish Yellow
		10	Little	Yellow	Greenish Yellow
		15	Good	Yellow	Green
		20	Good	Yellow	Green

(Continued)

Table 8. (Cont'd.) Effect of pH of Dyeing on Contrast

pH	Temp.	Time (Minutes)	Contrast	Color of Dyed Samples Treated	Untreated
3.5	175° F	30	Little	Greenish Yellow	Green
3.5	185° F	5	Good	Yellow	Green
		10	Good	Yellow	Green
		15	Little	Greenish Yellow	Green
		20	Little	Pale Green	Deep Green
		30	Little	Pale Green	Deep Green
3.9	165° F	5	Little	Yellow	Greenish Yellow
		10	Little	Yellow	Greenish Yellow
		15	Little	Yellow	Greenish Yellow
		20	Little	Yellow	Greenish Yellow
		30	Little	Pale Green	Deep Green
3.9	175° F	5	Little	Yellow	Greenish Yellow
		10	Little	Yellow	Greenish Yellow
		15	Little	Greenish Yellow	Green
		20	Little	Greenish Yellow	Green
		30	Little	Pale Green	Deep Green
3.9	185° F	5	Good	Yellow	Green
		10	Good	Yellow	Green

(Continued)

Table 8. (Cont'd.) Effect of pH of Dyeing on Contrast

pH	Temp.	Time (Minutes)	Contrast	Color of Dyed Samples Treated	Untreated
3.9	185° F	15	Little	Pale Green	Deep Green
		20	Little	Pale Green	Deep Green
		30	Little	Pale Green	Deep Green

Table 9. Effect of Varying the Proportions of Dyes Used

Dyestuffs		Contrast	Color of Dyed Samples	
Fast Acid Yellow G. S. %	Alizarine Sapphire F. S. %		Treated	Untreated
9	1	No Contrast	Yellow	Yellow
6	1	No Contrast	Yellow	Yellow
3	1	Good	Yellow	Green
4	1	Fair	Yellow	Yellowish Green
2	1	Little	Greenish Yellow	Green

Table 10. Effect of Dyebath Ratio on Contrast

Dyebath Ratio	Contrast	Color of Dyed Samples	
		Treated	Untreated
40:1	Little	Greenish Yellow	Green
60:1	Little	Greenish Yellow	Green
80:1	Good	Yellow	Green
100:1	Good	Yellow	Green

Table 11. Effect of Initial pH of Dyebath on Contrast and Levelness

pH	Contrast	Leveling	Color of Dyed Samples	
			Treated	Untreated
2.5	Little	Poor	Orange Red	Red
3.0	Good	Fair	Orange	Red
3.5	Good	Poor	Orange	Red
4.0	Little	Fair	Orange Red	Red

Table 12. Effect of pH Change During Dyeing on Levelness and Contrast

pH		Contrast	Leveling	Color of Dyed Samples	
Initial	Lowered to			Treated	Untreated
6.0	2.5	Good	Poor	Orange Yellow	Red
5.5	2.5	Good	Poor	Orange Yellow	Red
5.0	2.5	Good	Poor	Orange Yellow	Red
5.0	3.0	No Contrast	Poor	Orange Red	Orange Red

Table 13. Effect of Salt on Contrast and Levelness

pH	Glauber's Salt %	Contrast	Leveling	Color of Dyed Samples	
				Treated	Untreated
2.5	10	Little	Poor	Orange Red	Red
3.0	10	Good	Fair	Orange	Red
3.0	15	Little	Poor	Orange Red	Red
3.0	20	Little	Poor	Orange Red	Red
3.5	10	Good	Poor	Orange	Red
3.5	15	Little	Poor	Orange Red	Red
3.5	20	Little	Poor	Orange Red	Red
4.0	10	Little	Fair	Orange Red	Red

Table 14. Effect of Salt and a Change in pH on Levelness and Contrast

Initial pH	Contrast	Leveling	Color of Dyed Samples Treated	Untreated
3.5	Little	Poor	Orange Red	Red
4.0	Little	Poor	Orange Red	Red
4.5	Little	Poor	Orange Red	Red
5.0	Little	Poor	Orange Red	Red
5.5	Little	Poor	Orange Red	Red
6.0	Little	Poor	Orange Red	Red

Table 15. Dyes Used to Determine Range of Colors Available

Dyes Used						Temp.	Initial pH
Lower Group			Higher Group				
Name	Group No.	%	Name	Group No.	%		
Brilliant Scarlet 3R.	II	1	Milling Yellow NGS.	III	3	Boil	2.5
Brilliant Scarlet 3R.	II	1	Fast Acid Yellow GS.	III	3	150° F	2.5
Alizarine Sapphire SE.	I	1	Fast Acid Yellow GS.	III	3	150° F	2.5
Alizarine Sapphire SE.	I	1	Fast Acid Yellow GS.	III	3	Boil	2.5
Quinoline Yellow	I	0.5	Wool Fast Blue GL.	III	3	150° F	2.5
Quinoline Yellow	I	0.25	Wool Fast Blue GL.	III	3	150° F	2.5
Quinoline Yellow	I	3	Acid Brilliant Red GL.	II	1	150° F	2.5
Alizarine Sapphire FS.	I	1	Acid Brilliant Red GL.	II	1	150° F	2.5
Brilliant Scarlet 3R.	II	1	Milling Yellow NGS.	III	3	150° F	2.5
Brilliant Scarlet 3R.	II	1	Milling Yellow NGS.	III	3	160° F	3.2

Table 16. Dyes Used to Determine Effect of Relative Affinity on Levelness

Higher Group Dye		Lower Group Dye	
Name	Group No.	Name	Group No.
Milling Navy Blue 4B.	V	Fast Acid Yellow GS.	III
Milling Navy Blue 4B.	V	Brilliant Scarlet 3R.	II
Milling Navy Blue 4B.	V	Fast Wool Yellow 3 GL.	I
Milling Navy Blue 4B.	V	Fast Wool Red BL.	I

Table 17. Light Fastness

Dye(s) Used	Temperature of Dyeing	Fastness Rating (4)	
		Treated Sample	Untreated Sample
Fast Acid Yellow GS. Brilliant Scarlet 3R.	150° F	1	2
Fast Acid Yellow GS. Brilliant Scarlet 3R.	At Boil	4	4
Fast Acid Yellow GS. Alizarine Sapphire FS.	150° F	1	2
Fast Acid Yellow GS. Alizarine Sapphire FS.	At Boil	2	3
Brilliant Scarlet 3R.	150° F	2	4
Brilliant Scarlet 3R.	At Boil	4	4
Alizarine Sapphire FS.	150° F	2	4
Alizarine Sapphire FS.	At Boil	2	4
Resorcine Yellow	150° F	3	4
Resorcine Yellow	At Boil	4	4

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